

THE EXPERIENCE OF PETROBRAS WITH CHARACTERIZATION AND CLASSIFICATION OF DEPOSITED MATERIALS FOUND IN OIL PRODUCTION

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ABSTRACT

Experimental characterization of some deposited materials collected in Brazilian oil fields and transportation pipelines are presented, to point out limitations of data generated by fractional solubilization, which is normally employed for classification of deposits into paraffin waxes or asphaltenes. Gas chromatography, which is a reference technique for paraffinic materials, has its data compared to molecular weight by VPO, being clearly characterized the difficulties of elution for heavy fractions. It is also shown that most characteristic compositional properties for asphaltenes, like elemental analyses and aromaticity, are not conclusive for the definition of deposits as asphaltenic materials.

So, it is proposed that chemical analysis of deposited materials should aim ready classification of deposited material, since all of the techniques have limitations and yield information that should be considered qualitative and for comparison purposes. And since classification should be a way to provide quick responses to field problems, another concept was sought.

A classification technique based on thermogravimetry has been proposed to improve the capacity of PETROBRAS to determine the nature of some deposits verified in production equipment. It is based on the fact that asphaltenes yield considerable amounts of coke by pyrolysis, while paraffinic material do not. The method has been validated with several reference samples, and it is being used successfully in various field situations in Brazil

INTRODUCTION

Concerning to deposition problems, analytical techniques employed for characterization yield data to provide information about chemical nature of deposited material, which are also used to feed mathematical simulators of deposition used by production engineers. These computer programs support operational decisions that try to minimize or avoid deposition phenomena. Of course, due to the economical magnitude of problems brought by deposition, much is expected of these simulators, and therefore much is charged of analytical data. However, usual analytical techniques have some limitations, and careful interpretation of results is necessary.

Of course, it is normally easy to tell inorganic and organic (main focus of interest of this work) materials apart. And operational culture may be frequently employed for a successful pre-classification of organic ones into the two main classes normally recognized, i. e., paraffinic or asphaltenic deposits. In these cases, simulators may need some temperature or pressure dependent measurements, being a minimum characterization required. Sometimes, however, it is not possible to affirm anything previously. Our work has been showing this is the case of deposits found in production columns. Past experience shows that asphaltene precipitation frequently happens in pressure disturbance zones, mainly in bubble point regions of oils in production columns, as observed for example by IZQUIERDO and RIVAS (1995). Differently, paraffin deposition may possibly be observed in almost all pipes and tanks used in petroleum industry. So column deposits are an application of particular interest for any work on characterization, because both classes are possibly found. When the nature of deposited material is an uncertainty, its definition is the first necessary input. It should be remarked that, for analytical purposes, an operational definition for paraffin waxes or asphaltenes is based on solubility. It is normally accepted that paraffin waxes are a fraction insoluble in ketones at low temperatures (according for example to Shell SMS 1769) and asphaltenes are a fraction insoluble in light n-alkanes and soluble in aromatic solvents (according for example to IP-143). This definition may be used for classification of deposited material, being normally employed a sequential solubilization with a light alkane (which would solve paraffinic components) and an aromatic (which would solve asphaltenic components), as performed by ABUL FAZAL et al. (1995).

If further characterization is required, analytical techniques employed for deposited material are normally gas chromatography and nuclear magnetic resonance. Since they are both well known by analytical chemists, there is no need for considerations about their fundamentals. Interpretation of results from these two techniques are normally supported by other information, like elemental analyses or infrared spectra. It is impossible, however, to achieve a complete characterization, *stricto sensu*, of all components of deposits because there is an uncountable number of heavy components from

petroleum, and chemical analysis can not resolve heavy components.

Careful investigation of results obtained, shown below, indicates that these data may be inadequate for non equivocal conclusions about the nature of deposits. So, a new approach has been proposed, based on the fact that asphaltenes have large aromatic nuclei (BESTOUGEFF e BYRAMJEE, 1994). Those nuclei yield coke when pyrolysed, and this may be detected by thermogravimetry. This approach has been employed successfully for several field cases in Brazil.

EXPERIMENTAL

Sequential solubilization experiments were performed in a Soxhlet apparatus, and solvents chosen were n-heptane and toluene. After extraction, solvents were evaporated and weighed. All the procedure was repeated to constant weight with each solvent. Number molecular weights were determined by vapor pressure osmometry (VPO; a Wescan model 233 apparatus was employed), in toluene solutions at 88°C, with benzyl as a calibration standard. GC chromatograms were obtained in an HP 5890-2, with the following analytical conditions: 0.53 mm i. d. methyl silicon column (5 m length), programation for inlet temperature from 60 to 430°C at 70°/min, for the oven -20 to 430°C at 10°/min, then 5 min at final temperature, flame ionization detector at 430°C. TG curves were obtained in a DuPont 951 thermal balance with TA Instruments 2100 control system: 10 mg of sample heated firstly at 10°C/min up to 700°C under a 60 mL/min nitrogen flow, then at 10°C/min up to 1000°C under a 60 mL/min air flow.

RESULTS AND DISCUSSION

Sequential solubilization

To determine and follow the nature of deposited material found in the column production of a Brazilian off-shore well throughout 3 months in 1996, sequential solubilization was firstly employed. Samples were obtained on different days. Some samples demanded a 72 h reflux to constant weight, showing that even if the result is very conclusive, that procedure could not be considered practical. However, abundant insoluble material in both solvents was obtained, what makes impossible a classification by this approach. The presence of inorganics was considered, but low ash yields after burning did not confirm this possibility. Table 1 shows these results, which stress the need of further work in some cases.

Some possibilities were sought for a conclusive characterization. However, since deposits are normally complex mixtures, average parameters obtained by NMR, like amount of aromatic carbons (the most relevant one), are frequently found in intermediate values, which do not assign a clear classification, and the same happens to the C/H ratio from ultimate analysis. Fractionated precipitation and liquid chromatography (LC) show in some cases poor resolution of fractions obtained, and for LC fractions (normally saturates, aromatics, resins and asphaltenes) there is also loss of polar compounds that stay strongly adsorbed onto the stationary phase.

Gas chromatography and vapour pressure osmometry

An alternative that is very useful for several characterizations in petroleum industry is gas chromatography. So, the possibility of determination of paraffinic material by this technique was considered. Since one can accept two classes of materials in deposits, low contents of paraffins would characterize asphaltenic deposition.

Typically, a gas chromatogram of paraffinic material is similar to the picture presented in figure 1, for a paraffin wax obtained from a Brazilian oil by Shell SMS 1769/88. This oil was chosen for the study because it has deposition of paraffin wax proved by field experience. Clear separation is achieved for lighter linear alkanes, and peaks between them are attributed to other saturated hydrocarbons. In high temperature GC, this task is easily done up to 40 carbon atom alkanes, normally. After that, the number of carbon atoms after which no resolution is obtained (called in this work C^*) is a subjective parameter. If eluted material represented the whole sample, the distribution of linear alkanes and other components would be an important characteristic, since linear molecules have more ease to overlap their chains, propiciating deposition.

Table 2 shows main interpretation data for the chromatogram in figure 1, and, for comparison, for the GC analysis of a natural deposit. Naturally, one should expect that deposits would have longer components than laboratory precipitated paraffin wax, since this material was stable in oil before intervention, while the components of deposits were not. However, that is not what was found in the comparison, since the chromatogram of deposited material could be resolved up to 50 carbon atoms, while the other one could be up to 45, only, being also the amount of material up to C^* larger for the deposit. The non resolved fraction (from figure 1, one can consider after 60 carbon

atoms) was larger for the laboratorial wax. The only information that agreed with previous expectance was the ratio of linear alkanes to other components, which was slightly superior in natural deposit. The possibility of components of the oil that could be occluded in the natural deposit and would not be in the laboratorial one, because of washing by the ketone used as precipitant, was considered but not confirmed, since the first hydrocarbon present in both samples had the same carbon number, 16. These results are better explained in a comparison to molecular weight data by VPO. This technique, itself, yielded values of 554 and 506 for the number molecular weights of the laboratorial and natural waxes, respectively, leading to the same trend given by GC. However, from compositional distribution in the chromatogram, it is possible to obtain the molecular weight and thus a carbon number for a pseudo-alkane component that would represent the $C_{60}+$ fraction ($\#C_{60}+$). The equation for that is readily deduced:

$$M_n = 100 / \sum (\% / M_i) \quad (\text{Eq. 1})$$

where M_n stands for the average molecular weight of the whole deposit, and $\%$ and M_i for the weight fraction in the material and the molecular weight of each individual component, respectively. Using equation 1, one gets a value for $\#C_{60}+$ of 76 for the laboratorial wax, while for the natural deposit even an infinite carbon numbered pseudo component would yield the value from VPO. After substitution of all $\%$'s and M_i 's from the chromatogram of this sample, the value of M_n by equation 1 has a limit of 498 as the $M_n C_{60}+$ increases. One can deduce that non eluted material is much more representative for the natural deposit than it is for the laboratorial wax, and that evidences the limitation of GC for the analysis of field material. Qualitative analysis of eluted material does not help very much either, since it has been found that asphaltenes yield chromatograms similar to other petroleum fractions (AQUINO NETO et al., 1995).

Approach proposed - use of thermogravimetry

Based on the need of an approach that would not have all limitations detected by other techniques, we have conceived a quick experiment by thermogravimetry (TEIXEIRA and GONÇALVES, 1977). Basically the sample is heated under inert atmosphere, for distillation and pyrolysis of some constituents, then under oxidative atmosphere, which allows the burning of remaining material.

Behaviours of paraffins and asphaltenes submitted to those conditions were evaluated. Asphaltenes have as a remarkable characteristic relatively large alkyl side chains and aromatic nuclei (BESTOUGEFF e BYRAMJEE, 1994). We believe that branches may be thermally eliminated from the major structure, but aromatic nuclei will be thermally stable under inert atmosphere, maybe by the generation of coke. Paraffins should be either distilled or pyrolysed, so their TG would show different profiles in relation to asphaltenes, which would be enough since only classification of the predominant class of constituents of the sample is aimed. Inorganics would yield stable material at 1000°C under air, so they would be also evaluated.

TG would also have the advantage of analysis of the whole deposit without any pre-treatment, since water and excess occluded oil would be distilled before the temperatures of interest. It should be emphasized, however, that classification by the methodology studied necessarily presupposes that there are only the three possible classes cited above in deposited material, but that assumption is normally good for classification purposes.

Figure 2 shows a TG curve of a standard paraffin. It can be seen that before 700°C the distillation (or maybe pyrolysis) of the materials is already complete. In these TG curves, and in all the other ones in this work, mass loss is indicated by the monotonically decreasing curve, while the other curve is its first derivative. Figure 3 shows a TG curve of an asphaltene sample obtained by a standard method (IP-143), from which a typical profile of this class of material may be determined. There is effectively mass loss before air introduction, but the main remark, which will make possible the differentiation from paraffinic material, is mass loss after air introduction that is clearly seen. From these facts a classification scheme is proposed: paraffins are characterized by complete volatilization under inert atmosphere up to 700°C, asphaltenes by burning with air injection from 700°C, and inorganics by the burning residue at 1000°C.

The methodology has been employed for the classification of several real field deposits. Examples that prove consistency of the proposed approach are its applications to column deposits. Figures 4 and 5 show TG curves of two ones, from different wells from Brazilian fields, whose nature was found to be very distinct by the methodology proposed here.

CONCLUSIONS

Thermogravimetry may be used successfully to overcome a major problem in the study of

depositions, which is to reach a clear qualitative definition of the nature of deposited material. It does not yield properties of the deposits that are necessary inputs for simulation work, but it provides the ways to determine which phenomenon is to be modeled in each case.

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Table 1. Characterization of deposits of the same well (weight %)

Sample collected on	n-heptane solubles	toluene solubles	burning residue
January 11th	28.01	1.25	13.25
January 16th	2.85	6.31	11.65
February 9th	23.73	0.68	9.81
March 9th	24.39	1.16	5.62

Table 2. Comparison of a laboratorial paraffin wax of a Brazilian oil and a natural deposit

Sample	C*	%up to C*	%C ₆₀ +	%linear up to C* % other up to C*	#C ₆₀ +
Paraffin wax by Shell SMS 1769/88	45	55.53	27.53	1.83	76
Natural paraffinic deposit	50	69.01	11.90	1.93	∞

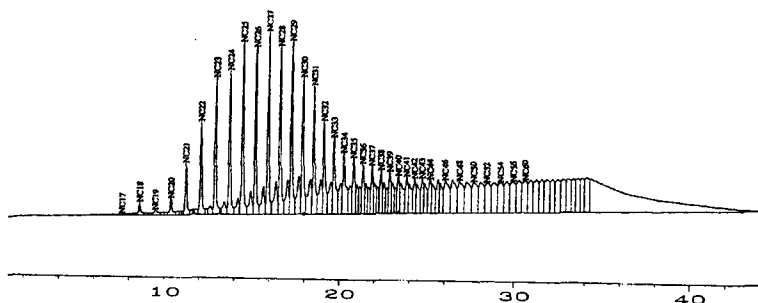


Figure 1. Gas chromatogram of a sample of laboratorial paraffin wax of a Brazilian oil

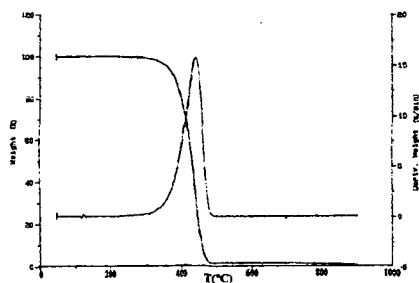


Figure 2. TG curve of a standard paraffin of average molecular weight 1000

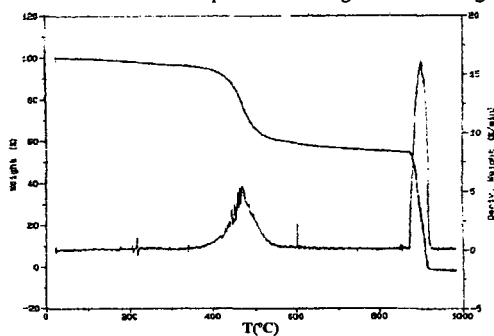


Figure 3. TG curve of asphaltenes from light arabian oil

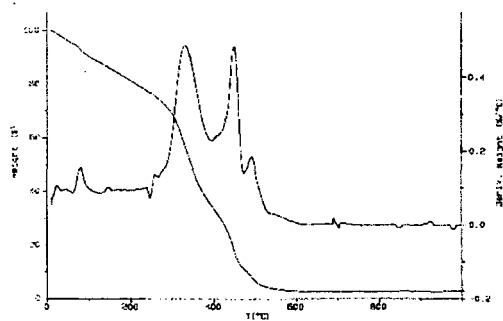


Figure 4. TG curve of a paraffinic production column deposit

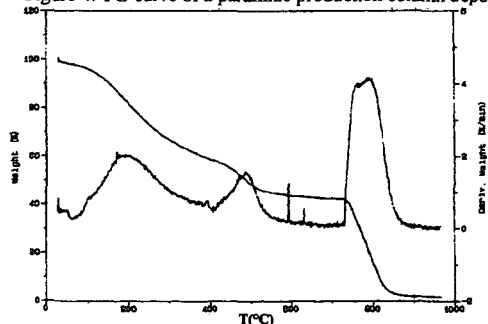


Figure 5. TG curve of an asphaltenic production column deposit